

**Raman Spectra of Calcium Silicate Hydrates Sorbing Iodine Ions in Saline Groundwater –
14077**

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ABSTRACT

The sorption behavior of I-127 (iodine-127) as an alternative of I-129 into Calcium Silicate Hydrate (CSH) gel existing in imitated saline groundwater (without drying process) was examined by using a Raman spectrophotometer and an Inductively Coupled Plasma-Atomic Emission Spectrometry instrument (ICP-AES). In the experiments, the Ca/Si molar ratios of CSH gel samples were set to 0.4, 0.8, 1.2 and 1.6, and NaCl concentration also was set to 0.6mol/L. These samples were synthesized with CaO, SiO₂ (fumed silica), and distilled water in a given combination under the condition of liquid/solid weight ratio 10, 15 or 20. The curing-times of CSH were set to 7, 14, and 30 days. Besides, the initial concentration of iodine was adjusted at 0.5, 5, or 50 mmol/L. The syntheses of all samples were conducted in a glove bag saturated with nitrogen gas. The sealed sample tubes were gently shaken with 120 strokes/min.

The Raman spectra of the samples showed that a CSH gel sorbed by iodide ions would undergo the depolymerization of silicate chain structures. That is, the silicate chain of CSH ($\equiv\text{SiO}-$) directly affects the sorption behavior of iodide ions into CSH gel. Furthermore, the amount of iodide ions retained in a CSH gel depended on initial concentration of iodide, curing-time, Ca/Si molar ratio and Liquid/Solid weight ratio. These results suggested that an altered CSH gel also might retard the migration rates of anion nuclides such as I-129 released from the repository system saturated with saline groundwater.

INTRODUCTION

CSH gel is a main hydrate of cementitious materials required for constructing the repository system of radioactive wastes. In Japan, the materials would also be used in order to solidify TRans-Uranium (TRU) radioactive wastes including a long-life nuclide I-129[1]. Since iodine ions undergo anion as mainly iodide ions, such nuclides strongly affect the annual dose rate evaluated in biosphere [2]. So far, the interaction of CSH gel and iodine ions has been examined by using drying CSH gel samples [3]. However, the repository system would be saturated with groundwater after the backfilling [2, 4]. Therefore, this study focused on the sorption behaviors of iodide ions onto CSH gel synthesized without drying process. While the CSH gel of ordinary Portland cement undergoes around 1.6 in Ca/Si molar ratio [5], an altered CSH gel decreases Ca/Si molar ratio through Ca-leaching with time. That is, we should consider Ca/Si molar ratio as an experimental parameter. Furthermore, saline groundwater might affect the chemical interactions of iodide ions and CSH gel [2] in comparison with fresh groundwater.

In this study, I-127(stable iodine) was used as an alternative of I-129. Considering a repository system saturated again with groundwater after backfilling, Ca/Si molar ratios of the CSH gel

samples were adjusted at 0.4, 0.8, 1.2 and 1.6 in sample tubes. For examining the influence of iodide ions upon the structure of a CSH gel, initial concentration of iodine was set to 0 mmol/L, 0.5 mmol/L, 5 mmol/L and 50 mmol/L by using a NaI solution. Furthermore, “hydration samples” (a NaI solution was added to a pre-cured blank CSH gel sample) are also prepared in order to study the sorption behavior of iodide ions after curing CSH gel. These results are compared with those of “co-precipitation samples” (a NaI solution was added before curing the CSH gel). Using the measurements of Raman spectra and some ion concentrations, this study discusses whether the CSH gel, formed as a secondary mineral around the repository, could retard the migration rates of anion nuclides such as I-129 released from the repository system.

EXPERIMENTAL

Samples

TABLE I shows a given combination to synthesize each CSH gel sample with CaO, SiO₂, and distilled water. NaCl solution (0.6 mol/L) was used as an imitated saline groundwater. SiO₂ (Fumed Silica, AEROSIL 300) was obtained from Japan AEROSIL Ltd. The specific area of BET (N₂ gas) was 300±30 m²/g. All of the other chemicals were obtained from Wako Pure Chemical Industries Ltd, and were used without further purification.

TABLE I. Materials Used to Synthesize Sample.

Liquid/Solid weight ratio	Ca/Si molar ratio	CaO [g]	SiO ₂ [g]	Solution [mL]
20	0.4	0.408	1.09	30
	0.8	0.641	0.859	
	1.2	0.792	0.708	
	1.6	0.898	0.602	
15	0.4	0.544	1.45	
	0.8	0.855	1.15	
	1.2	1.06	0.943	
	1.6	1.2	0.802	
10	0.4	0.816	2.18	
	0.8	1.28	1.72	
	1.2	1.59	1.42	
	1.6	1.8	1.2	

TABLE II summarizes the detail of CSH gel samples. For observing sorption behavior of iodine onto CSH, the four types of CSH gel samples were prepared by the following procedures: (1) a NaI solution is added before curing the CSH gel (hereinafter, referred to as “Co-precipitation sample”). Here, the concentration of iodide ions, i.e., [I⁻], is set to 0.5 mmol/L. (2) no NaI solution is added to

CSH gel sample (“I-free sample”). (3) a NaI solution is added after curing the CSH gel for 7 days (“Hydration sample”). Here, [I], is set to 0.5 mmol/L as in co-precipitation sample. (4) [I] is set to 0.5, 5.0 or 50 mmol/L in co-precipitation sample. Hereinafter, referred to as “Concentration-changed sample”. In TABLE II, the curing-time of “Hydration sample” means the contacting time (i.e., the reaction time) with iodide ions after curing the CSH gel samples.

TABLE II. Conditions of CSH gel Samples

Samples	Liquid/Solid weight ratio	Ca/Si molar ratio	Curing time [days]	Concentration of iodine	
Co-precipitation Samples	20, 15 and 10	0.4, 0.8, 1.2, and 1.6	7	0.5	
			14		
			30		
I-free Samples			7	0	
			14		
			30		
Hydration Samples			7	0.5	
			11		
			14		
Concentration-changed Samples			14		0.5
					5
					50

Procedures

All samples were adjusted without drying. This study followed some basic experimental procedures already reported by the authors [6]. In order to avoid contact with air, the synthesis of each sample was conducted in a glove bag saturated with nitrogen gas. The sample tubes were sealed and constantly shaken with 120 strokes/min. The temperature was kept constant within 298 ± 1 K. “Co-precipitation samples”, “I-free samples” and “Concentration-changed samples” were cured for a given time-period in the range from 7 days to 30 days. On the other hand, as mentioned above, “Hydration samples” were cured for 7 days before adding a NaI solution in the tube containing a CSH gel sample. Then, the concentration of iodide ions was initially adjusted at 0.5 mmol/L. The tubes were sealed again, and further shaken for 7 days, 11 days or 14 days.

After the above processes, a CSH gel sample was centrifuged for 10 minutes at 7500 rpm. Then, this study obtained Raman spectrum from a solid phase of the CSH gel sample. The spectrum was measured by a laser Raman spectrophotometer (JASCO, NRS-3300), where 532nm YAG (Yttrium Aluminum Garnet) laser was used for Raman scattering. Besides, the liquid phase of a CSH gel sample was filtered with 0.2 μm membrane filter. In the filtrated aliquot (liquid phase), the concentrations of Ca, Si, Na and I were measured by an ICP-AES (Seiko Instruments Inc.). Furthermore, using a pH-Eh diagram considering Na ions concentration, it was confirmed that the iodine in each sample exists mainly as iodide ions. The Eh values measured in each sample were in the range of +159 mV to +368 mV and the values of pH were in the range of 9.7 to 12.6.

RESULT AND DISCUSSION

Concentrations of Ca, Si and Na ions in the liquid phases

First of all, “the initially set Ca/Si ratio” and “the Ca/Si ratio after curing CSH gel” were confirmed in each CSH gel sample. Figure 1 shows the Ca/Si ratios of co-precipitation samples after curing CSH gel with I. Here, each ratio was evaluated by using the concentrations of Ca and Si measured in the liquid phase after curing time. As shown in Figure 1, the Ca/Si ratios of the solid phases were mostly maintained at the initially set ratios within the curing time. This study also confirmed that I-free samples, hydration samples and concentration-changed samples mostly maintained the initial ratios.

Figure 2 shows the concentrations of Na ions in the liquid phase of co-precipitation samples. As for the samples of 0.4, 0.8 and 1.2 in Ca/Si molar ratios, the concentrations slightly decreased with curing time. The decrease in concentrations seems that Na ions were sorbed and retained in the solid phase of the CSH gel. However, the sorption of Na ions was not apparently observed in the samples of 1.6 in Ca/Si ratio, while Funabashi et al. [6] reported that Na ions are exchanged with Ca ions in the CSH gel samples even if the Ca/Si ratio is relatively high.

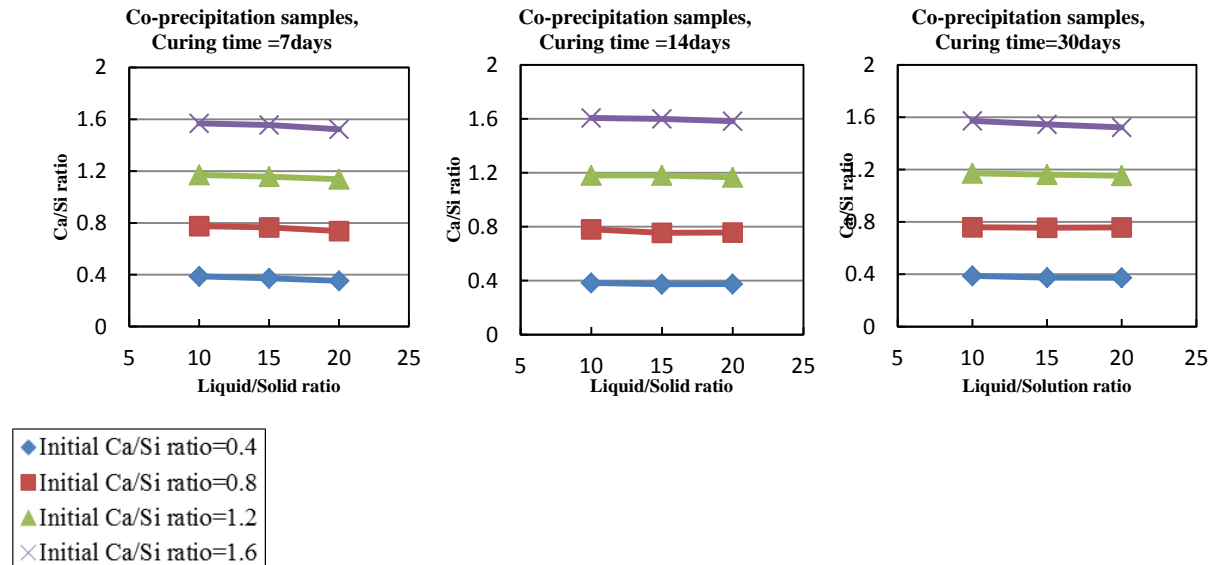


Fig. 1. Ca/Si ratio of the solid phase (Co-precipitation sample).

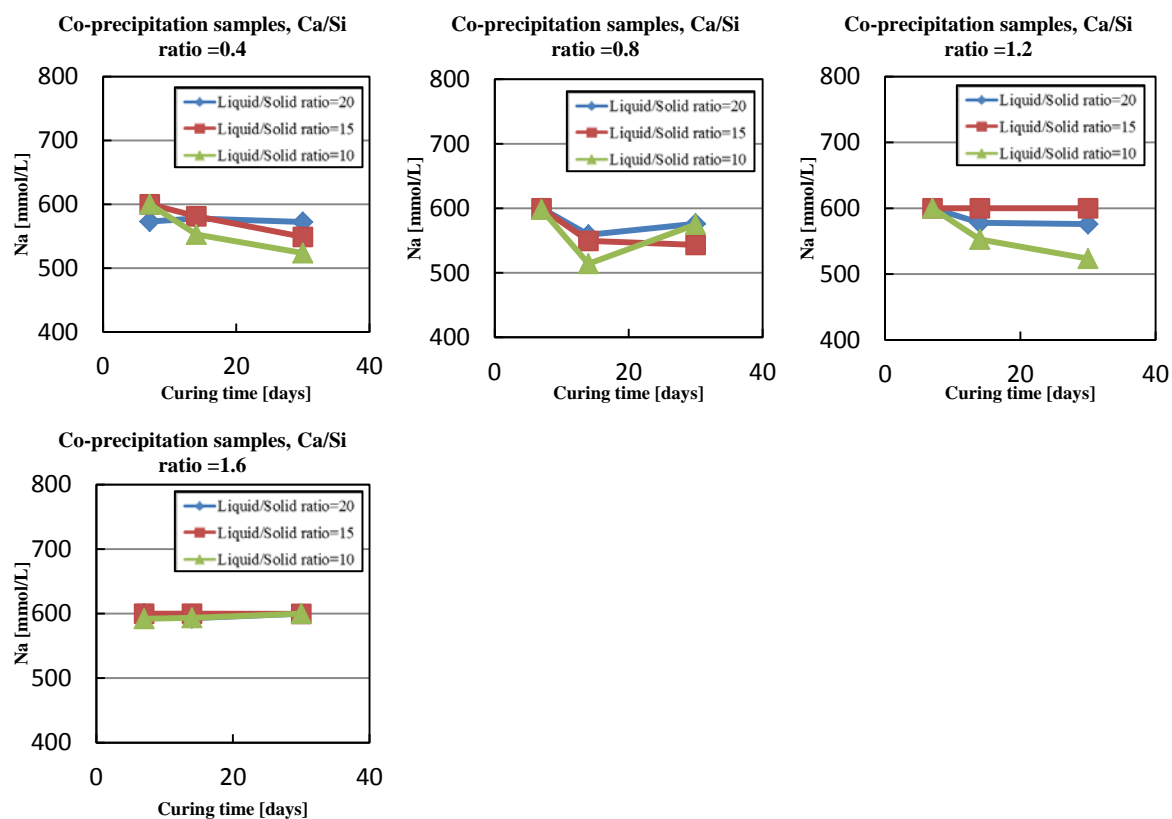


Fig. 2. Concentrations of Na ions in the liquid phase (Co-precipitation sample).

Amount of iodine in the solid phases

Figure 3 shows the amount (not concentration) of iodide ions existing in the liquid phases after curing each CSH gel sample. Since a part of the liquid phase (water-molecular) is hydrated in interlayers of CSH gel, such hydration also might play a key role in the sorption process of iodide ions into CSH gel. The amounts of iodide ions were calculated from a concentration of iodide ions and a volume of the liquid phase. The difference from the initial amount of iodide ions (red lines in Fig. 3) means the amount of iodide ions sorbed into CSH gel. Figs. 3 (a), (b) and (c) are the amounts of iodide ions of co-precipitation samples. As shown in Figs. 3 (a), (b) and (c), the sorbed amount of iodine to a solid phase depended on both the curing time and the Liquid/Solid weight ratio. That is, the sorbed amount became larger with curing time. Besides, as initial Liquid/Solid weight ratio decreases, the sorbed amount also became larger. Since the practical underground condition around the repository further limits the amount of liquid phase compared to these Liquid/Solid weight ratios given in this study, these results suggest more amount of iodide ions sorbed into CSH saturated with saline groundwater even if the CSH is altered to below 1.0 in Ca/Si molar ratio. On the other hand, Figs. 3 (d), (e) and (f) show the amount of iodide ions in hydration samples. Although the amount of iodine sorbed to a solid phase was relatively lower than those in co-precipitation samples, these results mean that the CSH gel contributes the stabilization of I⁻ even if a NaI solution is added after curing CSH gel.

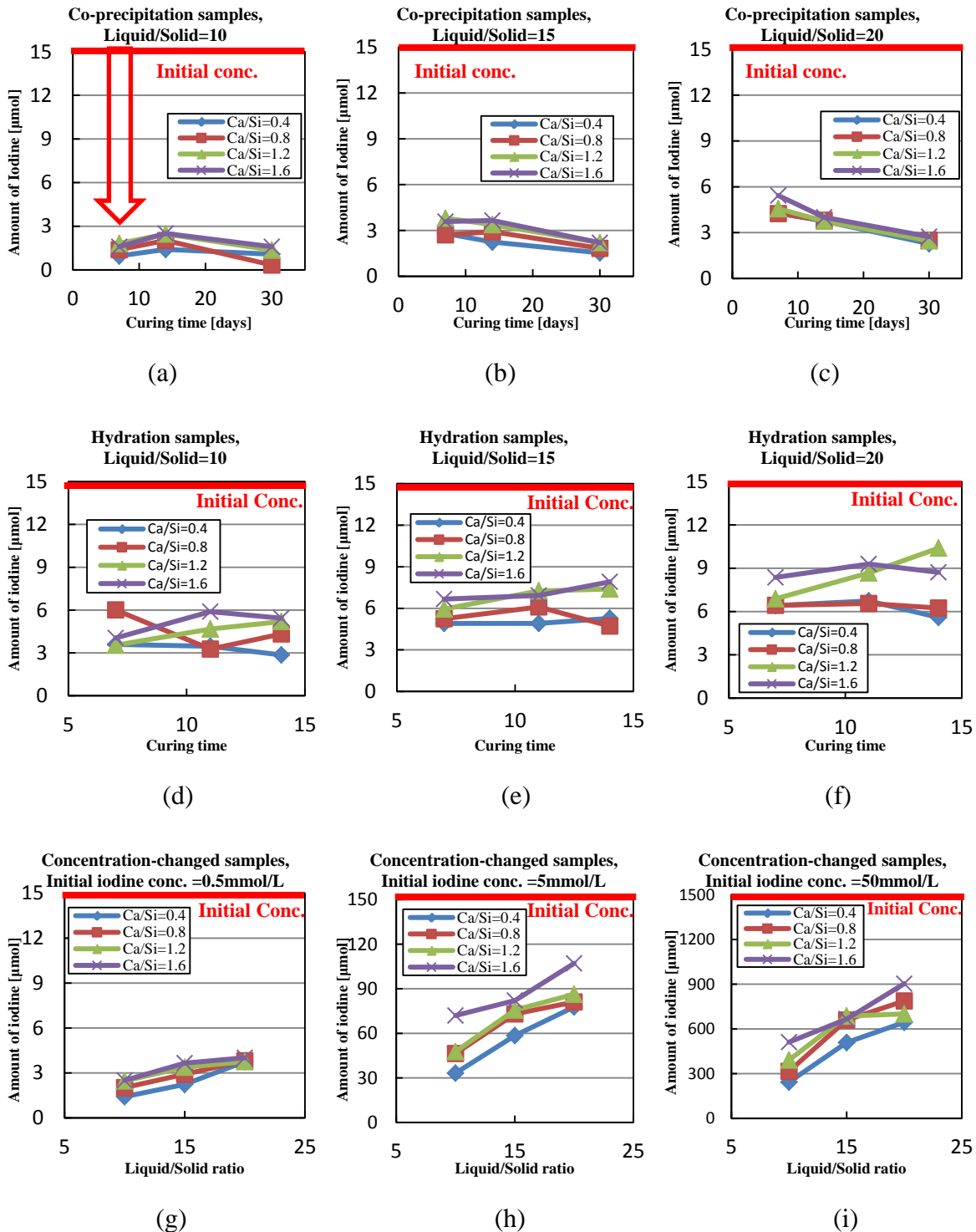


Fig. 3. Amount of iodine in the liquid phase ((a), (b), and (c) : “Co-precipitation sample”, (d), (e), and (f): “Hydration sample”, and (g), (h), and (i): “Concentration-changed sample”).

Since a hydration sample finally changes to a co-precipitation sample as a steady state, the curing time of 7 days to 14 days set in the hydration samples might be not enough to reach the steady state of CSH gel with iodide ions. Furthermore, Figs. 3(g), (h) and (i) show the amount of iodine in concentration-changed samples. In (h) and (i) (the initial concentration of iodine, 5 mmol/L and 50 mmol/L, respectively), almost half of the iodide ions was sorbed into CSH gel (the solid phase) regardless of the initial concentration of iodide ions. In other words, the sorption distribution coefficient K_d values of the samples were nearly constant within the range from 5 mmol/L to 50 mmol/L in the initial concentration of iodide ions. Here, the distribution coefficient K_d [L/kg] is described by

$$K_d = \frac{\frac{\text{amount of iodine in the solid phase [mol]}}{\text{weight of the solid phase [kg]}}}{\frac{\text{amount of iodine in the liquid phase [mol]}}{\text{volume of the liquid phase [L]}}}$$

Figure 4 shows the distribution coefficient K_d of the concentration-changed samples. In Fig. 4 (h'), (i') (initial concentration of iodine: 5 mmol/L and 50 mmol/L), the K_d -values were similar to approximately 1.0 L/kg. However, in Fig. 4 (g') (initial concentration of iodine=0.5 mmol/L), the value is around 3.0 L/kg. This result suggests that a CSH gel may change its structure due to the increment of [I⁻].

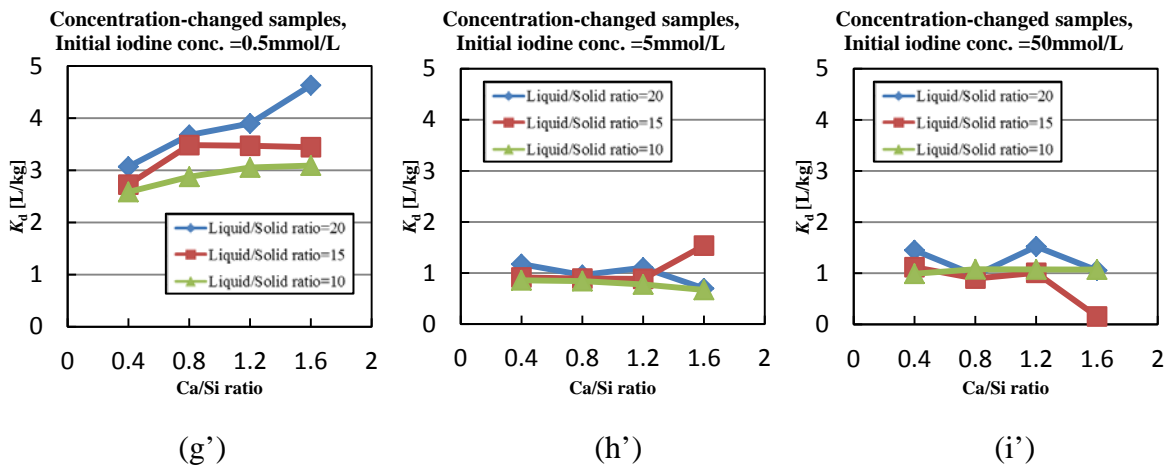


Fig. 4. Sorption distribution coefficient ((g') 0.5 mmol/L, (h') 5 mmol/L and (i') 50 mmol/L in concentration of iodine).

Raman spectra

From the results from ICP-AES measurements, the amount of iodide ions sorbed into a solid phase of CSH gel became larger with longer curing time. Besides, it was suggested that a CSH gel changes its structure, depending on concentration of iodide ions, even if the concentrations of Ca, Si and Na ions were almost constant in the liquid phase. Accordingly, this study examined

the structure change of CSH gel by using Raman spectra. So far, many studies have investigated the structure of a CSH gel, indicating that the structure of a CSH gel is similar to tobermorite [5, 7, 8]. Its main structure consists of hydrated Ca-O interlayer sandwiched between silicate chains [5]. Furthermore, the polymerization degree of SiO_4 tetrahedrons in silicate chains is described by Q^n units, where n is the number of bridging oxygen atoms [6, 8]. This study focused on the peaks of symmetric stretching vibration of Q^1 (870 cm^{-1}) and Q^2 (1010 cm^{-1}) in each Raman spectrum.

Figure 5 shows Raman spectra of I-free samples. While in low Ca/Si ratio samples (Ca/Si=0.4 and 0.8) the peak of symmetric stretching vibration of Q^1 were not detected, in high Ca/Si ratio samples (Ca/Si=1.2, 1.6), the peak were confirmed. In general, the intensity of Q^1 peak becomes stronger when Ca/Si ratio increases [e.g., 8, 9]. Such a tendency was also observed in co-precipitation samples and hydration samples. In this study, Q^1/Q^2 intensity ratios were used in order to estimate the depolymerization of the silicate chain. That is, when Q^1/Q^2 intensity ratio of a CSH gel sample exceeds the others, the Q^1/Q^2 intensity ratio means that the CSH sample is more depolymerized.

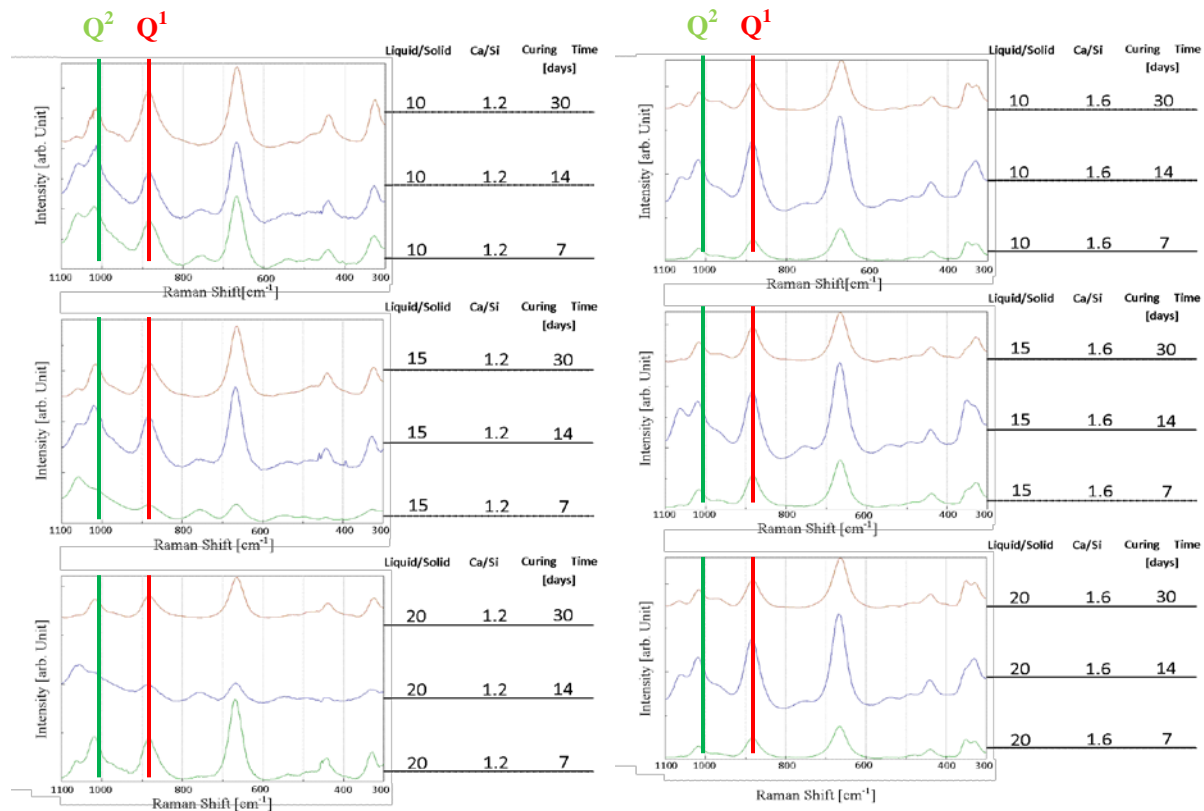


Fig.5. Raman spectra of I-free samples.

Figure 6 shows Q^1/Q^2 intensity ratios of I-free samples. The Q^1/Q^2 intensity ratios decreased once and increased with curing time, while the concentrations of Si, Ca and Na ions were also constant in the liquid phase of I-free samples as shown in Figures 1 and 2. That is, the Raman spectra suggest that a polymerization or a depolymerization process of silicate chain did not reach the steady state, even if the concentrations of Si, Ca and Na ions reach a pseudo steady state in the liquid phase.

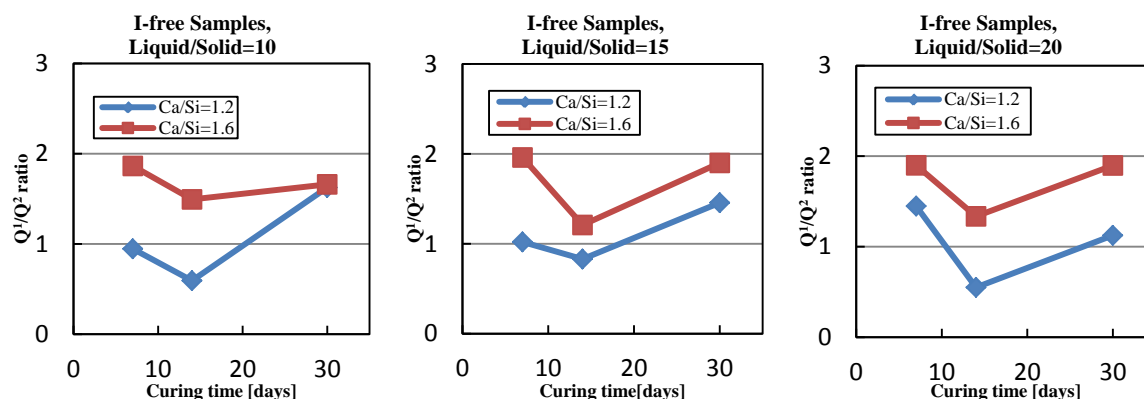


Fig. 6. Q^1/Q^2 ratio of I-free sample.

Figure 7 shows Q^1/Q^2 intensity ratios of co-precipitation samples. The Q^1/Q^2 intensity ratios decreased at the curing time of 7 days, in comparison with those of I-free samples (Figure 6). This means that a CSH gel sorbed by iodide ions underwent the polymerization of silicate chain in relatively early curing-time. Then, the Q^1/Q^2 intensity ratios increase with the curing time. On the other hand, the Liquid/Solid ratios did not remarkably affect the Q^1/Q^2 ratios, although a lower Liquid/Solid ratio sample could sorb more iodide ions. Besides, it was confirmed that the filtrated liquid amount increased with decrement in Liquid/Solid weight ratio. These results suggest that the hydration process (for forming CSH gel) also plays a key role in the sorption process of iodide ions into CSH gel.

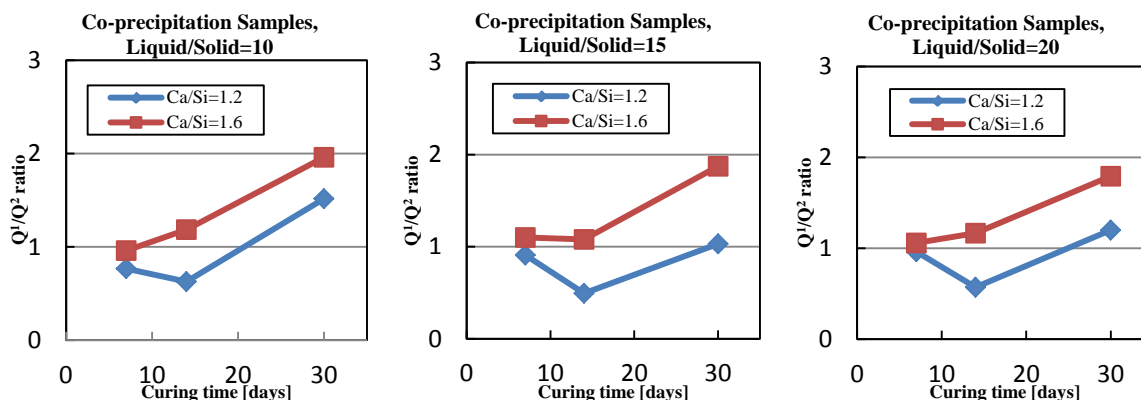


Fig. 7. Q^1/Q^2 ratio of co-precipitation samples.

Figure 8 shows Q^1/Q^2 intensity ratios of hydration samples. As shown in Figures 3 (d), (e) and (f) (in comparison with Figures 3 (a), (b) and (c)), it was suggested that the sorption processes of iodide ions to CSH gel were ongoing to the sorption state of the co-precipitation samples. Therefore, Fig. 11 means that the depolymerization processes of the hydration samples also were unstable, while the Q^1/Q^2 intensity ratios increase with the curing time of CSH gel.

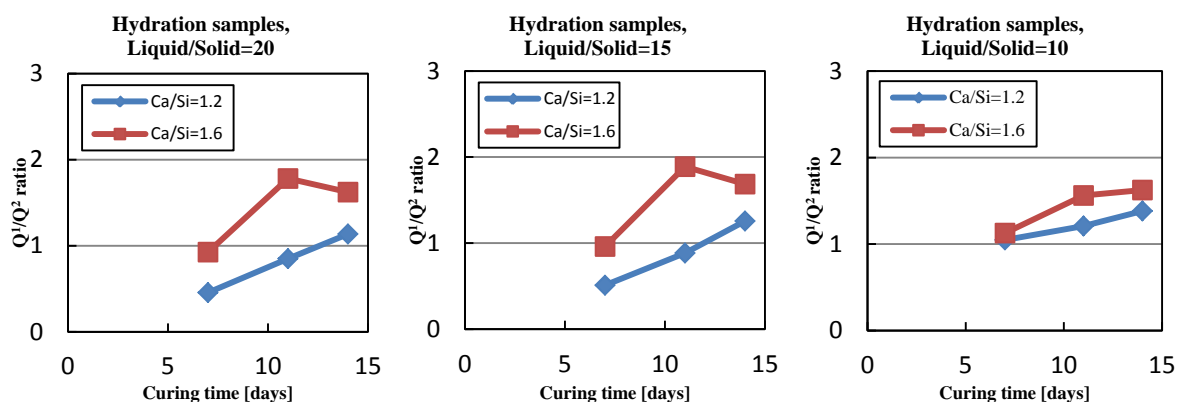


Fig.8. Q^1/Q^2 ratio of hydration sample.

Figure 9 shows the Q^1/Q^2 intensity ratios of concentration-changed samples, where the curing time was set to 14 days. The intensity ratios became larger with increment of the initial concentration of iodine ions. Besides, as shown in Figures 3 (g), (h) and (i), the sorbed amount of iodide ions increased with increment of the initial concentration of iodide ions. These mean that a CSH gel underwent the depolymerization with the sorption of iodide ions.

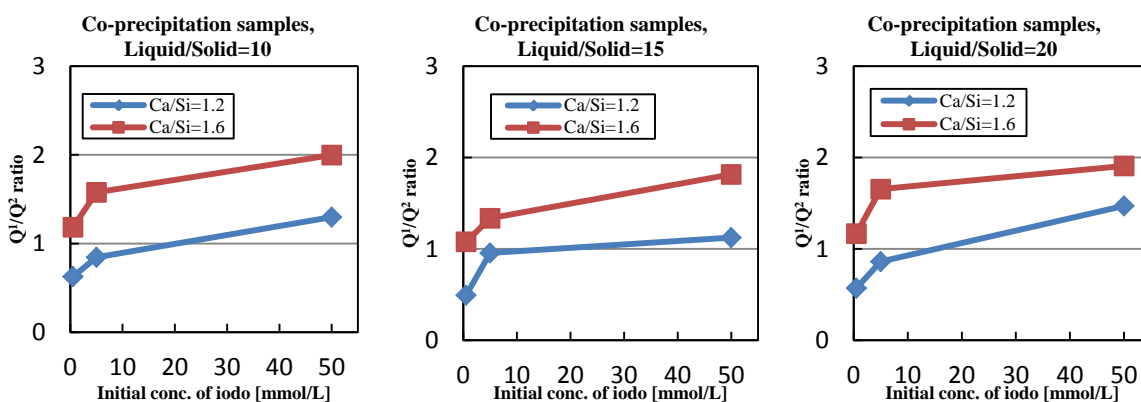


Fig.9. Q^1/Q^2 ratio of concentration-changed sample.

CONCLUSIONS

Considering the inflow of saline groundwater into repository, this study examined the interaction between CSH gel (without drying process) and iodide ions by using the concentration-changes of Ca, Si, Na and I ions and Raman spectra. In the results, the amount of iodide ions sorbed into a CSH gel depended on the initial concentration of iodide ions, curing-time, Ca/Si molar ratio, and Liquid/Solid molar ratio. Besides, the Raman spectra showed that a CSH gel sorbed by iodine ions would undergo the depolymerization of silicate chains, even if the concentrations of Si, Ca and Na reached a pseudo steady state in the liquid phase. These results mean that the silicate chain of CSH also affects the sorption behavior of iodide ions into CSH gel. Furthermore, when the Liquid/Solid weight ratio decreased, the sorbed amount of iodine apparently increased. Then, the filtrated liquid amount decreased with increment of Liquid/Solid weight ratio. Since the decrease of the liquid phase means the increase of the hydrated water in interlayers of CSH gel, such hydration processes also play a key role in the sorption process of iodide ions into CSH gel.

More reliable conditions around the repository further limit the amount of liquid phase compared to the Liquid/Solid weight ratios given in this study. Therefore, the results suggest that more amount of iodide ions is sorbed to CSH saturated with saline groundwater, even if the CSH gel is altered to below 1.0 in Ca/Si molar ratio. In general, the use of cement-based materials for the repository system alters the surrounding groundwater, exceeding 10 in pH for a time-period longer than 10^4 years [1]. Then, CSH gel is stably formed even if CSH gel undergoes a relatively low Ca/Si molar ratio. Therefore, the results in this study suggest that a CSH gel might retard the migration rates of anion nuclides such as I-129 released from the repository.

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